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Polyhedron 22 (2003) 2409–2414



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# Magnetic coupling in oxalato-bridged hetero-bimetallic compounds: an ab initio study

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Received 26 October 2002; accepted 13 January 2003

## Abstract

Multiconfigurational perturbation theory (CASPT2) and difference dedicated configuration interaction are applied to study the ferromagnetic coupling in oxalato-bridged Cr(III)Cu(II) molecular species, where the external ligands of the Cr(salen)C<sub>2</sub>O<sub>4</sub>Cu(acpy) complex, with salen = *N,N'*-ethylenebis(salicylideneaminato) and acpy = *N*-acetylacetonylidene-*N'*-(2-pyridylethyl)aminato, are modeled by simple H<sub>2</sub>O or NH<sub>3</sub> groups. The results show little dependence on the external ligand modeling. The experimental coupling is very well reproduced at both calculation levels when the model nearly reproduces the experimental geometrical structure. CASPT2 calculations on an oxalato-bridged Cr(III)Ni(II) model of Cr(salen)C<sub>2</sub>O<sub>4</sub>Ni(taea)BPh<sub>4</sub>, where taea = tris(2-aminoethyl)amine, are also in good agreement with experiment.

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**Keywords:** Ab initio calculations; CASPT2; Difference dedicated CI; Magnetic properties; Oxalato-bridged complexes; Hetero-bimetallic complexes

## 1. Introduction

Ligand-bridged hetero-bimetallic complexes can be used as building blocks to construct extended networks of high dimensionality that exhibit interesting magnetic behavior [1]. The interest of this type of compounds is due to the fact that both the ferromagnetic and the antiferromagnetic coupling between sites of different spin magnitude allows to achieve a net magnetization. From molecular complexes [2] to 3D networks [3,4], many oxalato-bridged bimetallic materials containing M<sup>II</sup>(C<sub>2</sub>O<sub>4</sub>)M<sup>III</sup> have been synthesized. Combined with bulky organic cations, 2D anionic layers of oxalato-bridged honeycomb structures have been obtained [5–7] that exhibit ferromagnetism or ferrimagnetism [8–10]. Recently, Coronado et al. [11] have obtained new bifunctional molecular materials by combining these magnetic inorganic layers with organic conductors. The presence of two cooperative properties in the same crystal lattice, ferromagnetism and conductivity in this

case, opens a large field of possibilities to the design and construction of supramolecular architectures combining different properties of technological interest. M<sup>II</sup>(C<sub>2</sub>O<sub>4</sub>)M<sup>III</sup> with M<sup>II</sup> = Cu, Ni, Mn, etc., and M<sup>III</sup> = Cr, Fe, Rh, Ru, etc., is the building block of these exciting materials.

Much work has been done from the seventies to interpret the origin, the magnitude and the sign of the magnetic coupling between transition metals across diamagnetic bridges. Based on Anderson's [12,13] considerations on the origin of the two antagonist ferro- and antiferromagnetic contributions to the coupling, qualitative [14,15] models were developed that have been applied to many homometallic binuclear complexes [16–18] to explain the trends of the coupling constant in front of the geometrical variations. From the first ab initio perturbative calculations performed on a series of biradicalar complexes [19,20] much theoretical work has been devoted to the magnetic exchange coupling. In the last decade, the broken symmetry Noodleman's approach [21,22] coupled with density functional theory (DFT) methods has been extensively used to calculate the coupling in binuclear systems [17,23–25]. Multi-reference wavefunction-based methods combined with perturbative or variational calculations within the

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CASPT2 [26,27] or the difference dedicated configuration interaction (DDCI) [28] schemes have shown to give excellent results on molecular systems [29–33] and on ionic solids [32,34–36]. All these systems are homometallic binuclear complexes, particularly Cu(II) binuclear systems. Only recently calculations have dealt with two different metallic centers [37,38].

Binuclear complexes provide excellent examples to check the validity of the theoretical approaches since the coupling constant can be accurately determined from experiments such as the variation of magnetic susceptibility with the temperature. Once the method is validated, higher dimensional systems can be modeled and studied. The present work applies the tools that have been successfully tested in the past on Cu(II) or Ni(II) dimeric systems to several models of two  $\text{Cr}^{\text{III}}(\text{C}_2\text{O}_4)\text{M}^{\text{II}}$  complexes [2]:  $[\text{Cr}(\text{salen})(\text{C}_2\text{O}_4)\text{Cu}(\text{acpy})]$ , with  $\text{salen} = N,N'$ -ethylenebis(salicylideneamine);  $\text{acpy} = N$ -acetylacetylidene- $N$ -(2-pyridylethyl)amine, and  $[\text{Cr}(\text{salen})(\text{C}_2\text{O}_4)\text{Ni}(\text{taea})]\text{BPh}_4$ , with  $\text{taea} = \text{tris}(2\text{-aminoethyl})\text{amine}$ . Both complexes were found to be ferromagnetically coupled with coupling constants of 5.6 and  $9.2 \text{ cm}^{-1}$ , respectively.

## 2. Computational information

Using the Heisenberg Hamiltonian  $\mathbf{H} = J\mathbf{S}_{\text{Cr}} \cdot \mathbf{S}_{\text{M}}$  with  $\mathbf{S}_{\text{Cr},\text{M}}$  the local total spin operators on the metal centers, the magnetic coupling parameter  $J$  is defined by the energy difference between two states of different multiplicity as  $E(S-1) - E(S) = SJ$ , with  $S$  the total spin of the system. Since the configuration of  $\text{Cr}^{\text{III}}$  is  $d^3$  and those of  $\text{Cu}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  are  $d^9$  and  $d^8$ , respectively, the spin coupling in these systems results in a quintet and a triplet state in the Cr–Cu system and in a sextet, a quartet and a doublet state in the Cr–Ni complex. The corresponding expressions for  $J$  are:  $J_{\text{Cr–Cu}} = 1/2(3E - 5E)$  and  $J_{\text{Cr–Ni}} = 2/5(4E - 6E)$ .

The bulky ligands of the complexes enforce the use of a model system. There exists a large amount of evidence in the literature that the replacement of the bulky ligands by appropriate smaller ligands hardly affects the calculated magnetic coupling parameters in wave function based methods [29,39–41]. Since the salen and the acpy ligands are coordinated to the metal by oxygen or nitrogen atoms, several models have been used for the Cr–Cu complex. The real external ligands have been substituted successively by seven water molecules, seven ammonia molecules, or three water molecules (two coordinated to Cr and one to Cu) and four ammonia molecules in the apical positions. The three model cations that have been calculated for this system are  $[(\text{H}_2\text{O})_4\text{Cr}(\text{C}_2\text{O}_4)\text{Cu}(\text{H}_2\text{O})_3]^{3+}$ , labeled hereafter as CrCu-1,  $[(\text{H}_2\text{O})_2(\text{NH}_3)_2\text{Cr}(\text{C}_2\text{O}_4)\text{Cu}(\text{H}_2\text{O})(\text{NH}_3)_2]^{3+}$ , CrCu-2, and  $[(\text{NH}_3)_4\text{Cr}(\text{C}_2\text{O}_4)\text{Cu}(\text{NH}_3)_3]^{3+}$ , CrCu-3.

Since the external ligands have shown very little influence on the results (see below), only one model has been used to represent the Cr–Ni complex,  $[(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Cr}(\text{C}_2\text{O}_4)\text{Ni}(\text{NH}_3)_4]^{3+}$ , CrNi. CrCu-1 and CrNi are represented in Figs. 1 and 2, respectively. In a first series of calculations, the models CrCu-1, CrCu-2 and CrNi have been calculated in the  $C_{2v}$  symmetry and CrCu-3 in the  $C_s$  one. The effect of the symmetrization has been only tested in CrCu-1 by distorting the ligand–metal bond angles and the oxalato-bridge geometry to tend to the experimental structure of  $[\text{Cr}(\text{salen})(\text{C}_2\text{O}_4)\text{Cu}(\text{acpy})]$ , although we keep the oxalato ligand in the plane. In the symmetrized models, the geometrical parameters have been averaged from the crystallographic data. The octahedral coordination of Ni in the Cr–Ni system makes the molecule more rigid and hence the real structure of this system is much closer to the symmetrized model. For this reason, no distortion has been considered.

Two different complete active space self-consistent field (CASSCF) wave functions [42] have been used as zeroth-order wave function for the CASPT2 calculations. First, a CASSCF wave function determined with a minimal active space including only the singly occupied orbitals, four orbitals with four electrons for the Cr–Cu systems, and five orbitals with five electrons for the Cr–Ni system. Defining the plane of the oxalato ligand as the  $xy$  plane and the  $x$  axis along both metals, these are the  $3d_{x^2-y^2}$ ,  $3d_{xz}$  and the  $3d_{yz}$  Cr orbitals and the  $3d_{xy}$  Cu orbitals for the Cr–Cu systems, and the  $3d_{xy}$  and

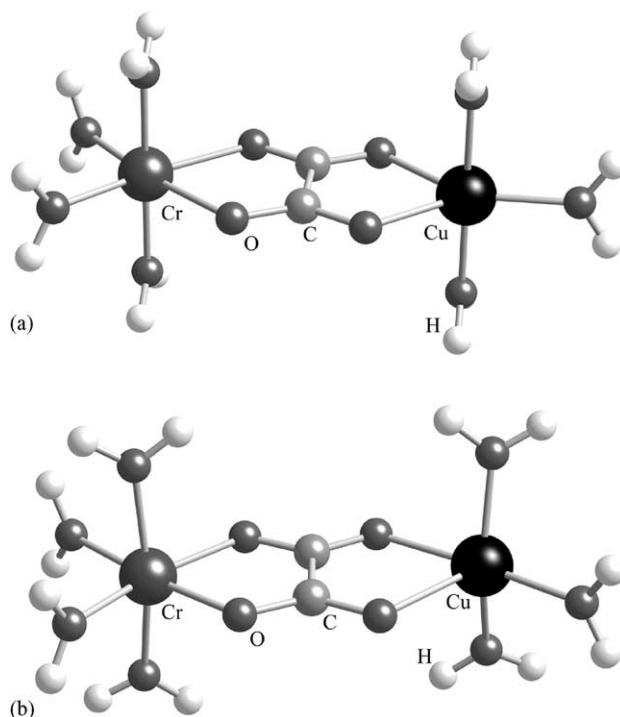


Fig. 1. Schematic representation of the  $[(\text{H}_2\text{O})_4\text{Cr}(\text{C}_2\text{O}_4)\text{Cu}(\text{H}_2\text{O})_3]^{3+}$  model. (a) CrCu-1; (b) CrCu-1\*.

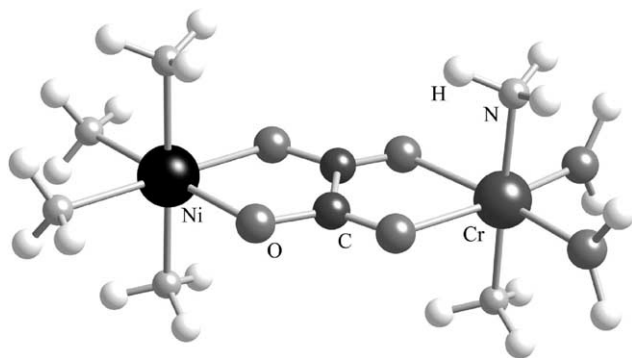


Fig. 2. Schematic representation of the  $[(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Cr}(\text{C}_2\text{O}_4)\text{Ni}(\text{NH}_3)_4]^{3+}$  model, CrNi.

$3d_{z^2}$  for Ni in CrNi. Second, a CASSCF wave function with an extended CAS that contains a virtual orbital for each singly occupied orbital in the previous CAS. For convergence reasons, one of the doubly occupied Cu-3d orbitals and its corresponding virtual must also be included in the active space [32]. The reference wave functions are labeled by CAS(4/4) and CAS(10/6) for the Cr–Cu systems, and CAS(5/5) and CAS(10/5) for CrNi. For CrCu-1, a larger CAS including the non-bonding oxalato pairs, labeled CAS(14/10) was also performed to check the consistency of the results. CASPT2 based on the extended CAS has recently been shown to reproduce rather accurately the exchange coupling parameters in a wide variety of biradicals, binuclear complexes and ionic insulators [32,43]. CASPT2 correlates all valence and semi-core electrons, i.e. the transition metal 1s, 2s and 2p electrons, and the C, N and O 1s electrons are not included in the correlation treatment. All calculations have been performed with the MOLCAS 5 code [44].

Some calculations have also been performed on the Cr–Cu system with the variational DDCI method [28]. DDCI is a selected multireference CI method. The minimal CAS defined in the previous paragraph is the reference space in both types of systems. The selection of the configurations is based on the understanding that up to second-order perturbation theory all configurations that arise from double excitations from the doubly occupied to the virtual orbitals do not contribute to the energy difference of the electronic states of interest and hence, can be eliminated. This largely reduces the computational effort. However, the CAS(4/4) reference still gives rise to huge CI expansions at the DDCI level. To overcome this difficulty, we have used the dedicated molecular orbitals (MO) strategy [45] to truncate the MO set. As pointed out by the authors of Ref. [45], the orbital energies do not give a good criterion to cut the orbital space, poor convergence was observed with the size of the MO space. Instead a sound hierarchic order of the MOs can be obtained by diagonalizing the difference of the two density matrices associated to the two states implied in the energy difference. The resulting

orbitals are known as dedicated orbitals and the corresponding eigenvalues, the so-called participation numbers, give an indication of the importance of each dedicated orbital in the magnetic coupling. In this way, the MO space can be reduced with almost no loss of accuracy. A final refinement of the method avoids the dependence of the results on the starting MOs by improving them iteratively (IDDCI) [46]. DDCI correlates the same electrons as CASPT2. Calculations have been performed with the CASDI code [47], dedicated and IDDCI orbitals are obtained with the NATURAL program [48].

The one-electron basis sets are of atomic natural orbitals type [49,50]. The following contractions have been used: (6s, 5p, 3d, 1f) for Cu, Ni and Cr; (3s, 2p, 1d) for C and O of the oxalato group; (3s, 2p) for N of the  $\text{NH}_3$  ligands and for O of  $\text{H}_2\text{O}$  ligands, and (2s) for H. It has been discussed in the literature [41,51–53] that there is little dependence of the results on the basis set in this type of systems. This basis set is of an intermediate quality and can safely be expected to give stable results.

In the DDCI calculations, the effective core potentials of Barandiarán and Seijo [54] have been used for the Cu and Cr atoms, where the valence electrons are described by a [9s, 6p, 6d]/(3s, 3p, 4d) basis set.

### 3. Results

The calculated coupling constant for the different models of the Cr–Cu system are reported in Table 1. The first result to be pointed out is that the CASSCF calculation gives the correct sign and order of magnitude of the ferromagnetic coupling, for all the models presented, although the coupling is underestimated. The ferromagnetic character of the coupling is easily interpreted from the orthogonality of the magnetic orbitals of both metals involved in the coupling, as pointed out in Ref. [2]. Fig. 3 shows the mainly  $3d_{xy}$  magnetic orbital of Cu and the mainly  $3d_{x^2-y^2}$  of Cr at the CASSCF level. A second conclusion is that the dynamical electron correlation slightly enhances the coupling and that both at the simple CASSCF and at the correlated CASPT2 levels the results show very little dependence on the active space. The result obtained at the (14/10) CASPT2 level for CrCu-1,  $6.3 \text{ cm}^{-1}$ , is nearly identical to that obtained with the (10/6) reference. This indicates that the bridge correlation is correctly treated by second order contributions.

Another important conclusion comes from the comparison of CrCu-1 to CrCu-3 results: the results show little influence on the external ligands. The results on the three models are quite similar although there seems to be a weak tendency to give smaller ferromagnetic interactions with stronger  $\sigma$ -donor character of the external ligands. The Mulliken population analysis from the

Table 1  
Calculated magnetic coupling constant  $J$  (in  $\text{cm}^{-1}$ ) for the Cr–Cu models at the CASPT2 and DDCI levels

Reference	CAS(4/4)			CAS(10/6)	
	CASSCF	CASPT2	IDDCI	CASSCF	CASPT2
CrCu-1	1.9	10.0	12.3	1.9	6.3
CrCu-2	1.3	5.7	–	1.6	7.5
CrCu-3	1.2	4.5	–	1.3	5
CrCu-1*	1.1	3.6	3.6	1.1	1

The reference CAS are indicated. The experimental value is  $5.6 \text{ cm}^{-1}$ .

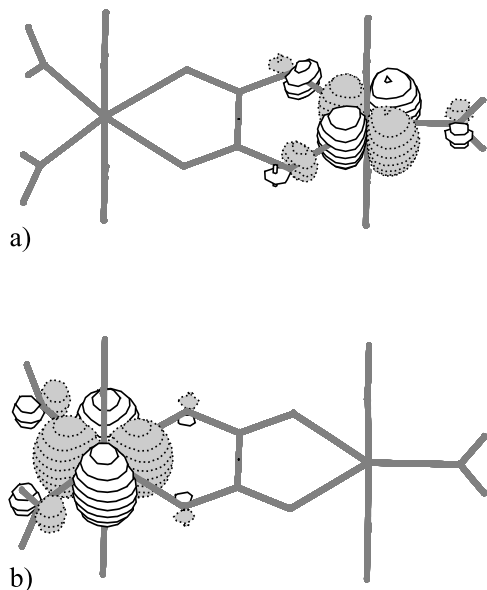


Fig. 3. Shapes of the magnetic orbitals of the CrCu-1 model at the CASSCF (10/6) level.

CAS(10/6), reported in Table 2, shows that the total metal electron population ( $Q$  in Table 2) significantly increases with the number of  $\text{NH}_3$  substituents but the effect of the substitution on the 3d Mulliken populations is much less pronounced, particularly in Cu. The higher donor character of the ligand has been invoked to interpret increasing antiferromagnetic coupling [55], but we observe that the effect on  $J$  is very small and after the inclusion of dynamical correlation no evident trend appears any more from the different models.

Table 2  
Mulliken population analysis of the Cr–Cu system at the CAS(10/6) level

	CrCu-1	CrCu-2	CrCu-3	CrCu-1*
$Q_{\text{Cr}}$	2.019	1.275	0.678	2.05
$Q_{\text{Cu}}$	1.324	0.962	0.767	1.327
$3d_{\text{Cr}}$	3.48	3.70	3.96	3.48
$3d_{\text{Cu}}$	9.12	9.13	9.14	9.14

Total charges,  $Q$ , and 3d Mulliken populations on the metal atoms.

When comparing the CASPT2 results with DDCI calculations performed in the CrCu-1 DDCI gives similar coupling constants. The calculated values with both CASPT2 and DDCI for the symmetrical models are all in a reasonable agreement with the experiment.

A more significant result is the trend observed for all level of calculations when the geometry is distorted from CrCu-1, a symmetrized  $C_{2v}$  geometry, to CrCu-1\*, a distorted geometry close to the experimental one. The modeling of the external ligands with seven  $\text{H}_2\text{O}$  molecules does not reflect the nature of the atoms coordinating the metals but from the preceding it is concluded that the effect of the external ligands is only minor. The coupling in the  $C_s$  structure decreases largely at the three correlated levels, but is also smaller at the CASSCF level. The Cu magnetic orbital gives the key to this phenomenon, as illustrated in Figs. 3 and 4. In the  $C_{2v}$  structure (Fig. 1(a)), the trigonal bipyramidal coordination of copper enforces that the magnetic orbital interacts with both oxygen atoms of the oxalato-bridge through a  $3d_{xy}$  orbital, as shown in Fig. 3(a), since both occupy equatorial positions. However, the geometry of the real ligand is close to a square basis pyramid, with one oxygen atom of the oxalato group in equatorial and the other in apical position, as shown in Fig. 1(b). The nature of the magnetic orbital is completely changed, as represented in Fig. 4. It gives a weaker interaction and smaller correlation effects on  $J$ , as shown from the difference between the CASSCF and the CASPT2 calculations in Table 1. From these considerations, it may be concluded that in this type of complexes the result is not strongly affected by the type of external ligands used in the model provided that the donor character is not dramatically changed. However, the

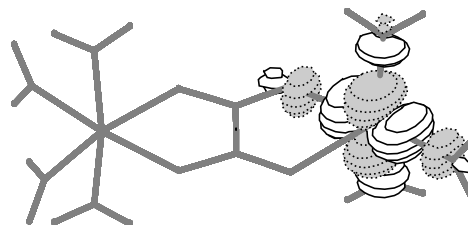


Fig. 4. Shape of copper magnetic orbital of the CrCu-1\* model at the CASSCF (10/6) level.



Table 3  
Spin densities of the CrCu-1\* complex calculated at the DDCI level

Cr	Cu	O <sub>Cr</sub>	O <sub>Cr</sub> (H <sub>2</sub> O)	O <sub>Cu</sub> (ax)	O <sub>Cu</sub> (eq)	O <sub>Cu</sub> (H <sub>2</sub> O)
2.92	0.86	0.03	0.00	0.01	0.06	0.03

The subscripts in the ligands indicate the coordinated. ax, eq indicate the apical or equatorial positions, respectively, of the oxalato ligand oxygen atoms.

location of the coordination atoms is much more important since it determines the nature of the magnetic orbital. The small influence of the external ligands on  $J$  has been found in previous systems [41] studied with the same multireference methods, although it is often not so in DFT calculations, probably because the DFT magnetic orbitals are more delocalized on the surrounding ligands [56]. The best result,  $J = 3.6 \text{ cm}^{-1}$  obtained at the DDCI level, is in good agreement with experiment.

The spin densities evaluated at the DDCI level have shown in ferromagnetic as well as in ferrimagnetic systems very good agreement with polarized neutron diffraction estimations [41,53]. The results obtained for the CrCu-1\* model are shown in Table 3 and corroborate the strongly localized character of the magnetic orbitals, even when the dynamical electron correlation, which introduces some delocalization to the ligand, is included. The spin densities on the bridge oxygen atoms are consistently very small, with only a significant value on the apical oxygen.

Table 4 shows the coupling constant at the CASPT2 level for the CrNi complex and the Ni magnetic orbitals are represented in Fig. 5. The same type of conclusions as for the Cr–Cu system emerge from the different calculations: practically no influence of the active space, an underestimation of the coupling at the CASSCF level and a good agreement with the experiment when the dynamic electron correlation is accounted for.

#### 4. Conclusions

The results presented in the present work on some models for heteronuclear systems suggest that ab initio wave function based methods can give valuable information about the magnetic coupling in more extended

Table 4  
Calculated magnetic coupling constant  $J$  (in  $\text{cm}^{-1}$ ) for the CrNi model at the CASPT2 level

CAS(5/5)		CAS(10/5)	
CASSCF	CASPT2	CASSCF	CASPT2
1.3	6.9	1.3	8.2

The reference CAS are indicated. The experimental value is  $9.2 \text{ cm}^{-1}$ .

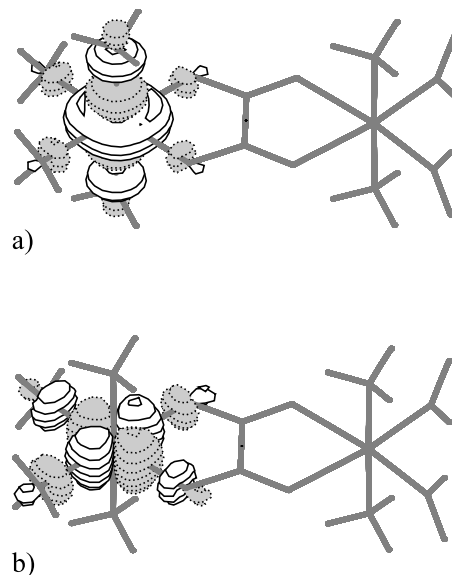


Fig. 5. Shapes of nickel magnetic orbitals of the CrNi model at CASSCF (10/5) level.

systems. CASPT2 and DDCI accurately reproduce the magnitude of the coupling in the oxalato-bridged Cr–Cu and Cr–Ni molecular systems analyzed through some models and indicate that a geometry of the model close to the experimental one is a more important factor than the choice of the model external ligands. The results are not very sensitive to the size of the active space used in the calculation and the minimal CAS including the magnetic orbitals and electrons seems to be sufficient to give reasonable values of the coupling. All these results suggest that the use of small external ligands, described with small basis sets, CASPT2 calculations with a minimal CAS and intermediate basis sets for the bridge and metal atoms can be a good strategy to analyze the magnetic coupling of many systems and to provide thus complementary helpful information on the behavior and on the design of novel systems.

#### Acknowledgements

Financial support has been provided by the Spanish Ministry of Science and Technology under Project No. PB98-1216-CO2-02, and the DURSI of the Generalitat de Catalunya (grant SGR01-00315).

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